INTERPRETING ELEMENTS AND ISOTOPES IN GLASS: A REVIEW

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Abstract

Substantial databases of elemental and isotopic analyses of ancient glass exist and are used to investigate raw material origin, trade, exchange and processes such as mixing and recycling. However, the chemistry of archaeological glass may be challenging for the untrained eye. This paper provides structured information on the origin of chemical elements and their isotopes in ancient glass. It details some of the functions of individual elements in the glass and from which raw material(s) or process(es) they originate.

Keywords

Glass, colourant, decolourant, flux, network former, periodic table

Introduction

Glass objects, mostly in the form of beads, are occasionally found in the archaeological record from the late third millennium BCE onwards. Nevertheless, it took until the Late Bronze Age (sixteenth-fifteenth century BCE) before regular and controlled glass production was active in the major ancient centres of the Near East, Egypt and the Mediterranean. Glass at that time was strongly coloured and intended as a high status material, equivalent to semi-precious stones. At the end of the Late Bronze Age, and the second millennium BCE, considerable social change spread across the Mediterranean area with the collapse and disappearance of the great states of the time. This is believed to have affected dramatically the glass industry with a breakdown of trade and exchange networks. Glass becomes relatively rare, but reappears by the tenth to ninth century BCE, again initially rarely, and generally in the form of strongly coloured beads or vessels. Significantly, this new glass also has new raw materials leading to a new composition. The invention of glass blowing somewhere in the first century BCE and its rapid spread throughout the Roman Empire makes glass a daily, utilitarian, commodity by the first century

AD. By then, strong coloured glass has been largely replaced by weakly coloured (blue and green) and colourless glass, used as an everyday household material. Glass in Byzantine, Islamic, medieval up to modern times essentially remains the same: a translucent, lightly coloured or colourless everyday material.

It is generally accepted that raw glass was widely traded, for example as ingots of coloured glass in the Late Bronze Age or as chunks of colourless or naturally coloured glass in the Roman and early medieval periods. In this way, glassmaking sites are separated from glass shaping or forming sites. Much like with ceramic studies, questions asked in glass research relate to the type of raw materials used, the technology and provenance of the produce, and reconstructing trade, exchange and recycling. These studies are tackled through the chemical analysis of glass objects or raw materials which run alongside longstanding work on typology of vessels shapes, for example.

In terms of raw materials, the great majority of ancient glass was chemically based upon silica or (much later and rarer) lead, fluxed with soda or potash to lower the melting temperature. The earliest known soda (-lime-silica) glass was found in Late Bronze Age Mesopotamia and Egypt and continued as the dominant compositional type of glass across Western Asia and the Mediterranean right up to the modern period. Potassium-rich glasses are confined largely to medieval Europe and to Asia. The manufacture of colourless lead-based glass has been largely restricted to tablewares, and mostly from the seventeenth century CE onwards, though Han dynasty Chinese, Roman and Islamic high lead (opaque) glass exists. This paper does not aim to cover the whole area of glass production, it would be impossible to do so in the length allowed. It covers as many compositions as it can, and draws examples mostly from the Mediterranean World.

Specific compositions of glass indicate certain sources, technical processes and periods. Concentrations of major elements allow glass types and raw materials to be identified. Substantial databases of major, trace element and isotopic analyses of glass exist (e.g. Brill 1999, Brill and Stapleton Brill, 2012, Degryse 2014), and are used to investigate trade, exchange and technical processes such as mixing and recycling. As the elemental chemistry of archaeological glass may be challenging for the untrained eye, this paper aims to assist in this by discussing the function of individual elements in the glass and where they originate. Basic information on the nature and origin of chemical elements and their isotopes in glass is provided, and references to further examples and applications in literature are given.

Glass flux types: Na, K (with Rb, Cs), Mg, P, B, Sr, Cl, S

To lower the melting temperature of the network former, silica, in a glass to temperatures easily achieved in ancient technological processes, a flux or melting-aid has to be added. Mixed with the silica, soda or potash work well as a flux, forming a so-called eutectic melt. In ancient soda-lime-silica glass, two major types of flux are used, defining two major categories of glass (Sayre and Smith 1961): (1) plant ash glass, combining a plant ash with quartz pebbles and (2) natron glass, combining soda-rich evaporitic minerals with quartz sand.

The ashes of beach and desert plants were used as flux in the earliest glass from the LBA onwards for more than a thousand years, to produce what is widely called plant ash glass. The most essential characteristic of the plants used is the presence of high contents of sodium carbonate or bicarbonates, and possibly hydroxides. Especially suitable for glassmaking are the salt resistant plants growing in semi-arid or saline maritime environments. Examples mentioned in literature are the genera *Salicornia* and *Salsola* of the Chenopodiaceae family (Tite et al., 2006; Henderson, 2013a, b). Other types of plants may also have been used for LBA and IA glass making, possibly providing ashes higher in potash, used as the flux source in so-called mixed alkali glass (Tite et al., 2006). Most late Bronze Age glasses reach soda levels between 14 and 20 wt.%. Accompanying elements in the plant ash include significant input of silica and lime (CaO), with elevated Mg, K and P contents and significant other accessory and trace elements(for instance Rb and even Cs, which have a high affinity with K) (Freestone, 2006). LBA glass made with halophytic plants are called ‘high magnesium-high potassium (HMHK)’ glass, while their mixed alkali equivalents are termed ‘low magnesium, high potassium’ (LMHK) glass. However, the relationship between the chemical composition of certain plants, their ashes and the glasses produced from them is complex. This is caused by various factors, the most important ones being the geochemical composition of the soil on which the plants grow, the use of (parts of) specific plant species and genera, and the ashing and melting conditions before and during glass production (Henderson, 2013a, b).

Mineral soda (*natrun* or natron, mainly lake deposited sodium carbonates such as natron and trona. but often mixed with sulphates and other salts such as burkeite or halite) gradually took over the function of flux in the early first millennium BCE. Natron glass was the predominant type of ancient glass in the Mediterranean, Europe and the Near East west of the Euphrates, from the middle of the first millennium BCE until the ninth century CE (Freestone et al. 2002a; Shortland 2004). To the east, plant ash was continued to be used as flux, probably reflecting the lack or poor availability of natron or raw natron glass there (Shortland et al. 2006). Natron or sodium carbonates in their pure form do not occur in nature frequently. An overview of the known sources of natron in antiquity is given in Shortland et al. (2006), pointing to Egypt, and most likely the Wadi Natrun and al-Barnuj, as the main supplier of natron in the ancient world, hereby corroborating the words of Pliny the Elder (Nat. Hist. XXXI, 111). To date, however, there is no direct evidence that soda coming from the Wadi Natrun was exported for glass production outside Egypt. Moreover, one also needs to be aware of the enormous amounts of natron used in glass production, and it is uncertain whether the Egyptian lakes could on their own supply these vast quantities. Devulder et al. (2015) have demonstrated the presence of natron deposits in the whole of northern Africa, and have suggested the possibility of their use alongside the Egyptian sources. Elementally, natron deposits are very pure, and beside soda contribute very little to the final glass composition. Boron (B) is brought into natron glass mostly from the flux, and the B isotopic composition of evaporites has been used to try to distinguish different sources of this raw material (Devulder et al. 2014, 2015). B shows a wide spread in its isotopic composition in nature and has proven useful in the geochemical provenancing of evaporates in geology. Rarely, ancient high B glass (> 1000 ppm B) has been recorded, where B plays an important role in compositional grouping and provenancing such glass (cf. glass network former).

Around the 9th century CE, perhaps due to difficulties in the supply of natron throughout the Mediterranean and Europe, plant ashes once again became dominant flux (Freestone 2006), using varied sources of ash. While Venetian glass makers monopolize the import of Syrian plant ashes similar to the earlier Bronze Age glass raw material, in northern Medieval Europe glass makers experiment with the use of ashes of wood (in particular beech ,e.g. Wedepohl and Simon 2010) or the use of mixed alkali (e.g. Wedepohl et al. 2011) or even fern, bracken or kelp as a flux (Dungworth, 2012; Dungworth et al., 2009).

As for major and minor constituents of glass, the elements Mg, K and P separate plant ash based glasses (now interpreted as all plant ashes, from halophytic plants to wood, fern, bracken, kelp…) from natron based glasses, also called 'low magnesium-low potassium' (LMLK) glass. Usually, contents higher than 1.5% in both MgO and K_2O are thought to indicate the use of plants as a flux, while P_2O_5 contents may reach close to 1% in plant ash glasses. Along with HMHK and LMHK glasses, an additional subdivision may usefully be recognised for post 9th century plant ash glass (Freestone 2006). Plant ash glasses from the Syria-Palestine region have compositions with K_2O and MgO of 2-3.5% (e.g. from the Serçe Limani wreck, Brill 1999; Banias, Freestone et al. 2000; and Tyre, Freestone 2002), while plant ash glasses made up to the seventh century A.D. to the East of the Euphrates, in the region of the Persian Empire under the Parthians and Sasanians, tend to have MgO and K_2O contents greater than 3.5 %. However, a difficulty in resolving plant ash glass provenance is that our understanding of the manufacture of this type of glass is very limited.

The earliest wood ash fluxed glass, also known as *forest* glass, produced in Medieval Europe in a few initially heavily forested areas, is likely made with beech and other woods or bracken with high but variable contents in potash, soda, magnesia and lime (Dungworth, 2012). A further glass type with a very high lime content, as in so-called High Lime Low Alkali (HLLA) glass, has also been tentatively assigned to the use of wood ash (Dungworth, 2011). Kelp glass can be recognized by its very high (> 1000 ppm) strontium contents (Dungworth, 2012). For (post) Medieval plant ash glasses Wedepohl and co-workers (Wedepohl and Simon 2010, Wedepohl et al. 2011, 2011b) suggested a series of trace elements specific to the wood ash used in glass production (Sr, Rb, Zn, Ni, Cu, B, Ba, Mn), might offer the potential to characterize such glass from certain regions.

Almost all fluxes contain quantities of chlorides or sulphates. These are unwanted, because of their practically non-reactivity in the glass batch (Tite et al., 2006), and can form immiscible glasses on top of the silicate glasses beneath. They enter the glass composition in limited amounts (0.5 to 1%), but rarely more. By the mid nineteenth century CE, the production of synthetic soda through the Leblanc process becomes common, and goes on to provide the bulk of the flux used in the modern glass industry (Dungworth, 2012). The use of this synthetic soda produces a soda-silica-lime glass with low potassium content and little to no phosphorous or chlorine, a useful marker for modern glass compared to historical or ancient.

Glass stabilizer: Ca, Mg, Sr

The eutectic mixture of network former and flux in a glass needs to be stabilised by lime and/or magnesia. Without stabilising elements, the resulting glass is soluble in water, a property not usually desirable in man-made vitreous materials. In plant ash glasses, it is usually thought that no additional lime needs to be added as it is sufficiently present in the plant ash itself (Barkoudah and Henderson, 2006). However, cuneiform glassmaking texts do suggest that lime might be added in addition (Shortland, 2012). In later natron based glasses, however, the mineral soda, introduces virtually no lime into the glass batch. Consequently, lime in natron glass is mainly derived from particles of shell or limestone, either added on purpose or naturally occurring in the silica source (Freestone, 2006). Another, unintentional, incorporation of lime might happen by the partial dissolution of the crucible linings used into the glass batch, or through contamination by fuel ash (Shortland, 2012).

The concentration of Sr in natron glass artefacts is a useful indicator of the form in which the lime source was added during production. Due to their similar atomic radius, Sr substitutes for Ca in Ca-rich minerals, in particular calcite and aragonite. Aragonitic shells and marine biogenic carbonates contain relatively high concentrations of Sr (Wedepohl and Baumann, 2000): values fluctuate between 8000 and 1200 ppm Sr for respectively aragonite and calcite in equilibrium with seawater. In contrast, diagenetic alteration means that Mesozoic and Palaeozoic limestones only contain a few hundred ppm Sr. As a consequence, a low Sr content of less than 200 ppm in the final glass points to the use of geological limestone, while higher Sr concentrations between 300 and 600 ppm suggest the use of (Holocene) beach shell fragments. Some other elements, such as Mg, Fe, P and Mn, could potentially be incorporated into glass via the lime source, but only at very minor levels (< 0.1 wt.%). Also, most trace elements and REE only occur in negligible amounts in lime sources compared to the concentrations commonly found in sand used as a silica source (Wedepohl et al., 2011b; Brems and Degryse 2013), so once again the lime source will not bring significant amounts of these elements into the glass. In relatively modern glasses, the evolution of manufacturing techniques between the two World Wars, saw replacement of a proportion of the calcite based lime in glass by dolomite based lime and magnesium. This is helped to overcome devitrification problems (Dungworth, 2012).

The application of strontium isotope analysis in research on ancient glass depends primarily on the assumption that the strontium in the glass is incorporated with the lime-bearing constituents (Wedepohl and Baumann 2000). It has been assumed that the contribution of natron to the strontium balance of glass is negligible (Freestone et al. 2003), and minor contributions may be attributed to non-quartz minerals in the silica raw material (Freestone et al. 2003, Degryse et al.

2006). Where the lime in a natron glass was derived from recent beach shell, the strontium isotopic composition of the glass is close to that of modern sea water (Wedepohl and Baumann 2000, Freestone et al. 2003). Where the lime was derived from geological limestone deposits, the Sr signature in the glass is a reflection of seawater at the time this limestone was deposited, possibly modified by diagenetic alteration (Freestone et al. 2003). Plant ash glasses are likely to have been produced from low-lime sand or (pure) quartz pebbles (e.g. Henderson et al. 2005). In this case, strontium in the glass is derived from the plant ash, the isotope ratio thus reflecting the bio-available strontium of the soil in which the plants grew. This, in part, reflects the geological origin of the soil (Freestone et al. 2003). Both the strontium isotopic ratio and strontium concentrations are thus useful indicators. Strontium concentrations in plant ash glass often show a considerable variability, indicative of the varied or complex source of the strontium and the concentrating effect of ashing the plant (Henderson et al. 2005, Barkoudah and Henderson 2006). Henderson et al. (2009) illustrate how important it is to establish variations in Sr isotope signatures in the landscape as part of trying to provide a provenance for plant ash glasses. A first survey of the Sr isotopic composition of glass throughout the ancient world has indicated its use in classifying glasses of the World according to their origin (Brill and Fullagar 2006). The effects of recycling on the strontium isotopic composition of glass have been studied by Degryse et al. (2006). In this study, mixing lines and a plot of isotope signatures versus concentrations demonstrated that the Sr in a local, glassworking site was a mixture of the signatures of two imported end members.

Glass network former: Si, O, Al, Fe, Ti, Cr, Zr, REE with Nd, Pb (with Ba) et al.

Tracing the silica source is a good starting point for provenancing ancient glass, since makes up the bulk of the glass, c. 60 to 75 wt.% in all but high-lead glasses. Potential sources include coastal and inland sands, quartz pebbles and other geological deposits such as vein quartz, chert or quartzite. Quartz pebbles are a relatively pure source of silica (Shortland, 2012). Only a few elements may be incorporated into the crystal structure of quartz and then only in trace quantities. Nevertheless, quartz pebble deposits regularly contain upwards from 0.5 wt% of Al_2O_3, Fe_2O_3 or TiO_2, usually in the form of associated iron (hydr)oxides or clay minerals. In contrast, a silica sand source can contain a wide range of minor and trace elements associated with the different accessory minerals mixed with the quartz sand through common geological and geographical processes (Wedepohl et al., 2011, 2011b). Elements like iron, titanium and alumina are usually related to the concentrations of specific minerals (feldspars, clays…) in the sand. Concentrations of lime and alumina are sometimes used for subdividing natron glasses into groups, as these elements reflect the silica and lime source (be it as separate constituents or as one sand raw material, Freestone et al. 2000).

Some elements are strongly concentrated in specific minerals while other elements are taken up in minor amounts into non-quartz or heavy minerals. Examples of elements that concentrated into their own minerals are Zr in zircon, Ti in rutile, ilmenite or titanite, Ba in barite and Cr in chromite. Their distribution is mainly controlled by heavy mineral concentration processes (Degryse and Shortland, 2009). Through the same processes, other detrital minerals from weathered ore deposits, such as galena (Pb) or sphalerite (Zn) might contribute their particular metal in the final glass composition (Wedepohl et al., 2011). Elements like Ca, Fe, Mg and Al enter the glass batch with minerals such as feldspars, clay, pyroxene, amphibole, mica and calcite, commonly occurring in sand. Feldspars have K-, Na- and Ca-rich compositions. Ba, Rb, Cs and Sr can be related to these and other silicate minerals, substituting for the alkali or calcium (Brems and Degryse, 2013). The presence of elements like Sc, V, Cr, Co and Ni is usually related to the occurrence of iron oxides or olivine. Hf and Y are mostly found in the heavy mineral zircon while Nb occurs in rutile. Th and La are dispersed throughout the mineral monazite, and B is an important constituent of tourmaline. Also the elements Li, P, Mo, Cs, Bi, Th and U in glass are probably related to the sand raw material (Brems and Degryse, 2013, and references therein). The observation that 25 minor elements (Be, Sc, V, Cr, Ge, Y, Nb, REE (La to Lu), Ta, W and Bi) occurred in almost equal concentrations in all subtypes of wood ash glass, was interpreted as the fact that these elements originated from the silica source of the glass (Wedepohl and Simon 2010).

Trace elements in glass can help to separate compositional groups and assign individual objects to them, although the application of trace elements in glass provenancing so far has remained limited. De Raedt et al. (1999) have studied the provenance of Venetian and façon de Venise glasses 16th-17th century CE glasses, while Freestone et al. (2000 and 2002b) and Aerts et al. (2003) have investigated trace elements as more specific indicators of origin of Roman to Byzantine/Islamic glass raw materials. Trace element analysis has been most successful in provenancing LBA plant ash glasses (Shortland 2005, Shortland and Eremin 2006, Shortland et al. 2007, Walton et al. 2009). Analysis showed trace element variations in especially Ti, Zr, Cr and La contents, allowed glass from Egyptian sites to be distinguished from that found on Mesopotamian sites. These differences may reflect varying plant ash compositions between the two areas, differences in silica source compositions and/or contamination of the melt by clay or grinding debris (Shortland 2005; Rehren and Pusch 2005; Shortland *et al.* 2007).

Rare Earth Elements (REE: La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu) are used to distinguish sand raw materials from various geological environments. In such studies, REE compositions are normalised to the Earth's continental crust composition, and described as enriched or depleted compared to the average crust, this in contrast to other studies, where REE concentrations are normalized to values in chondritic meteorites. However, in quartz-rich sands, the REE are mainly concentrated in the clay and silt fraction, and earlier studies have indicated that only fundamental changes in regional geology would result in different REE profiles (Degryse and Shortland, 2009; Walton et al., 2009). Within the REE, Nd is inherited in glass from the non-quartz mineral content of the silica raw material used. Since as no high Nd glasses are known in the archaeological record, the effect of glass recycling on the Nd composition of a glass batch is thought to be not significant and will not change significantly with the addition of colourants or opacifiers. This means that Nd isotopes offer great potential in tracing the origins of the silica in primary glass production and therefore the glass itself. Since the initial paper by Degryse and Schneider (2008), several groups have applied Nd isotopes to trace the silica sources of early Bronze Age to Roman and Byzantine glass production around the Mediterranean. A full review of the use of Nd isotopes in reconstructing the Greco-Roman glass economy is detailed in Degryse (2014).

O isotopes were one of the first systems to be applied to provenancing ancient vitreous materials (Brill, 1970). There is a natural range in isotopic values of quartz sands and quartz veins or pebbles depending on their geological origin, e.g. erosion from magmatic rocks, hydrothermal formation, metamorphic conditions. It is stated by Brill (1970) and Brill et al. (1999) that the O isotopic composition of ancient glass will be mainly dependent on the silica source, as it is the predominant component, with minor influences of flux and stabiliser. However, the use of O isotopes in recent studies has been limited, possibly because of the large overlaps in isotopic signature between many possible silica sources for ancient glass making (Leslie et al. 2006, Silvestri et al. 2010).

As mentioned above, exceptional glass compositions with very high boron and alumina contents have been recognized. In general, a high alumina composition is commonly associated with India and Southeast Asia more widely (Brill, 1987). The study of Dussubieux et al. (2010) of Indian glass found in Africa, south Asia and southeast Asia revealed a wide variety of alumina-rich glass compositions. Glass with alumina concentrations in excess of 4 wt% in combination with boron >500 ppm are rare in ancient times (Rehren et al., 2015; Schibille, 2011; Conte et al., 2016; Purowski et al., 2012), but occur over two millennia in Turkey and parts of Europe. They are thought to be associated with a possible Turkish production location, although it is not known whether the considerable boron amounts are derived from the sand or the flux, and the exact location of their origin has not yet been proven.

Lead glass occurs in Han China (2nd century BCE to 3rd century AD), and differs significantly from the contemporaneous western silica-natron glass tradition. Lead takes up the function as network former, flux and stabilizer in this glass type, instead of silica, soda or potash and lime. This glass typically also contains several weight percent barium. The late date for making glass in China may suggest that the technology was brought from the Middle East along the Silk Road (Fuxi et al. 2009), but the fundamental difference in technology could indicate an autonomous development. High Pb glasses in the West are rare, but some high Pb Roman glass does exist. In medieval and later Europe, lead glass was used as a base glass for mosaics, enamels, stained glass and also in glazes, while lead was added to Islamic plant ash glass in Spain to produce a particular composition (Duckworth et al. 2015). Colourless lead-based (crystal) tableware only occurs from the seventeenth century CE onwards (Dungworth, 2011).

Classic glass colourants and associated elements: Co, Cu, Sb, Pb, Mn, Sn, As, Zn, Ni, Ba

The most striking feature of ancient glass is often its colour, obtained naturally or intentionally via the use of (de)colourizers and a careful control of furnace parameters, and resulting in a wide variety of hues (Jackson 2005). Some minor elements in ancient glass are typically associated with the intentional colouring or decolouring of the material, such as Sb for opacifying or decolouring, Mn for decolouring or a purple colour, Co for a deep blue colour, Cu for blues, blue/green or red colour, Sn for an opaque white appearance etc (Henderson 2000), Pb with Sb or Sn for opacified yellow glasses. Such elements are often added as separate constituents in the form of ores (e.g. stibnite), minerals (e.g. alum), metals (e.g. bronze) or an intermediate compound derived from them and have a wide range of associated (trace) elements. In certain circumstances, the use of minerals to (de)colour a glass will have a significant effect on the compositions of those elements present in the material, and hence these elements can no longer be used to provenance the silica or flux raw material, or should at the very least be treated with the necessary caution. Moreover, while the element Cl in ancient glass is usually considered to enter the glass batch with the flux material, S can originate from the flux or sulphate/sulphide ores used as (de)colourants.

Co is one of the strongest coloring elements, with 0.10% CoO enough to colour a glass a distinctive blue. Co is also one of the most useful in that the element commonly occurs in its ore with a range of other elements such as Fe, As, Mn, Ni, Zn, Bi and others. These associated elements are often carried into the glass with the cobalt pigment, and often act as a trace element fingerprint which can indicate the Co ore source. In some cases, the Co pigments, often transported as a glass colorant called “smalt” can travel large distances. European smalt Co pigments have been indentified in the enameled procelains of 18th century China, for example (Giannini, et al, 2017). See Gratuze (2013) for a good summary.

Sb was widely used as an opacifier in glass from the Late Bronze Age onwards. Calcium antimonate (white) and lead antimonate (yellow) are commonly found, while Sb was also added to blue glasses to achieve opaque turquoise (Shortland, 2012). Interestingly, Sb gains a second use as a decolourant in the Greco-Roman period, until replaced by Sn-based opacifiers or Mn-based decolourants around the 4th century CE (Tite et al., 2008). The most likely raw materials used are Mn and Sb bearing minerals, such as pyrolusite (MnO_2) and stibnite (Sb_2S_3). Sn can be added as cassiterite (SnO_2) or could come from bronze scrap or more generally copper alloys (associated with As or Sb). Sb ores may also bring As to a glass batch, while Ba may be introduced through the Mn-bearing mineral used as a decolourizer (or as an impurity in the sand), associated with mineral such as e.g. psilomelane. Mn decolouring of glass has been known to influence the Sr isotopic composition of the glass (Ganio et al. 2012). Despite the fact that many analytical studies have been devoted to decolourizing agents, compositional analysis has not been able to reveal the provenance of the ores used, although the Causasus has been suggested (Shortland 2002). A new way to investigate the provenance of Sb in glass is by isotopic analysis, for which the analytical methods have recently been developed (Lobo et al. 2014). This approach may help determine the origin of Sb in early glass artefacts, where it is used as an opacifier, possibly following the development of Sb metallurgy in the Caucasus during the Bronze Age (Degryse et al. 2015).

The largest share of ancient translucent glass from Greco-Roman times onwards, has a blue-green colour owing to Fe impurities introduced into the glass via the raw materials (Jackson 2005), usually in the form of silicates other than quartz or as iron oxides. The iron content of the glass may then be associated with such elements as Ti, Zr or Cr. An increasing popularity of colourless glass can be observed from the early Roman period (1st century AD) onwards. Colourless glass can be produced either by selecting raw materials that are low in iron minerals (high-purity sands) or, more commonly, by the addition of a decolourizing agent. Sb is a more efficient decolourizer than Mn and results in a more brilliant glass, likely by removing dissolved gases (Jackson 2005).

An important factor to take into account in the analyses of trace elements in ancient glass is the fact that the presence of elevated contents in metals such as Pb, Zn or Cu may indicate that scrap glass, including small quantities of coloured glass or metal coated glass, was incorporated in a glass batch, pointing to 'recycled' material. The (trace) elemental composition of an ancient glass can be easily altered by mixing raw materials, recycling of scrap glass or the addition of mineral matter as a separate constituent to the glass batch, complicating any interpretation of glass analyses.

Weird and wonderful glass colourants: Au, Cr, Cd, Se, U

Whilst many of the colorants discussed above have been widely used across the World to create coloured glasses and, indeed, glazes, and may well have been independently discovered in more then one place, other technologies, particularly the later more modern ones, are very likely to have been discovered only once. They are severely limited in time frame and usually geographic spread and therefore are very useful for dating and provenancing glass. Au was used in high status glass from the 3rd century CE in Rome (Walker 2018). Here it is sandwiched in the glass as Au leaf between two glassy layers. However, more importantly for this paper, Au can be used in another form to colour the glass itself. This is colloidal Au, trace amount of Au nanoparticles that colour the gold a distinctive ruby colour. An early, famous version of this is the Lycurgus Cup, dating to the 4th century CE (Freestone, et al. 2007). The technology for using Au in this way in glass and glazes seems to spread widely, certainly as far as China. It continues to be used in modern glass, including "cranberry glass" (named for its colour) which is coloured this way.

Other element used in colouring glasses are the result of experimental work conducted in the nineteenth and twentieth centuries that aimed to isolate new elements and exploit them commercially, Cr, Cd, Se and U are all examples of this and produce a range of colours including greens, yellows, oranges and reds depending on their oxidation states (Weyl 1951, Newton and Davison 1989).

Mixed origin: Pb isotopes

As can be seen from above, Pb can enter a glass in measurable quantities from a range of different raw materials and for a range of different reasons, deliberate and not deliberate. Pb isotopes are therefore discussed separately here. Pb isotope ratio analysis has been applied to a range of archaeological vitreous materials, in particular by Brill and co-workers (1974, 1979, 1991) and Barnes and co-workers (1986). In these studies, it was possible to distinguish between vitreous materials in different regions; however, some overlap was noted between ‘fields of origin’, and this became a standard problem with Pb isotopes (as with O isotopes discussed above). In further studies, Pb isotopes were used with varying success to link raw material mixtures or regional signatures to glass production units (discussed in Degryse *et al.* 2009). Low Pb concentrations in glass, in the 10 to 100 ppm range, are likely to originate from heavy or non-quartz mineral constituents in the silica source (Wedepohl and Baumann 2000), though such low levels of lead have also been ascribed to recycling (Henderson 2000) or to impurities in plant ashes used as a flux (Barkoudah and Henderson 2006). The discovery of a homogenous lead isotopic composition in a range of glass samples is likely to suggest that a homogenous silica raw material has been used for the manufacture of that glass, and perhaps that it was produced at a single location (Degryse *et al.* 2005). Heterogeneous Pb isotopic compositions of a range of glass samples, particularly with moderate Pb contents between 100 and a few thousand ppm, are an indication of recycling of the glass, while a linear trend in Pb isotopic composition may be indicative of the mixing of two or more end members to produce a glass type (e.g. Degryse *et al.* 2005, Freestone *et al.* 2005). Moreover, the recycling of glass has typical chemical consequences. The incorporation of old coloured and opaque glass into a batch, with each cycle of re-use, will lead to a progressive increase in the concentration of colourant elements such as copper and antimony, but also lead (cf. *supra*, Henderson 1995, Jackson 1997). Recycled glass may have up to a few thousand ppm of lead, which evidently will entirely alter the lead isotopic composition of the glass, and delete its original raw material signature. Though lead isotopes may help to trace silica sources used in glass and glaze production, clearly caution is needed in *interpreting* the results.

Very high Pb concentrations (>1wt%) are usually caused by the addition of a mineral compound to the glass batch as a colourant, usually obscuring the original signal of the sand raw material. Work on provancing Pb colorants is ongoing, and suffers from the problems of overlapping provenance fields that have plagued Pb isotopic work on copper alloys.

Difficult and understudied: Ga, Ge, Ta, Re, Os et al.

There are a range of elements that do not fit into the above categories. Particularly the use of (LA-)ICP-MS to analyse ancient glasses has led to large table of data and the identification of some elements in the glasses for the first time. Little work has to date been done on these elements and there significance within the glass is unclear. Examples include Ga and Ge, which are present in many glasses at tens of ppm level, but do not seem to indicate source or production technology. More data (and more serious thought) on these elements might show them to be useful indicators, but at this point little progress has been made.

A final mention should be made of the elements that are not so far covered here. The capability of measuring such other elements exists, however, at the moment most groups working on ancient glass do not routinely analyse for them. For some elements, such as I and Br, this is understandable since they are difficult to measure. Others, in particular the heavier transition metals (Ta, Re, Os, etc.) could be measured, but very rarely are. Perhaps they would show no discernable patterns (they are likely to be present only as a few ppm at the most), but only trying them would show one way, or the other.

Conclusion

Glass is a complex material, and ancient glasses particularly complex. One of the reasons for this is that ancient raw materials are seldom pure. Incorporating a desired element, for example soda as a flux, inevitably brings in a host of more-or-less unwanted other elements. Additionally, some elements in glasses originate not from one raw material, but potentially from several. Interpreting patterns in these elements, which is a routine job for a glass specialist in archaeological science, requires a knowledge of which elements are likely to co-occur and therefore what their likely source might be. Identifying their presence allows the interpretation of what effect they might have on the characteristics of the glass. This paper gives the background to many of these elements, to show how they have been used in ancient glasses and how interpretations of source, provenance and technology have been drawn from compositional data. However, it has also pointed out that there is still a long way to go with understanding all elements The main reason for this is the availability of low detection limit techniques (especially LA-ICPMS), which has opened a new window particularly on the trace element compositions of ancient glasses.

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